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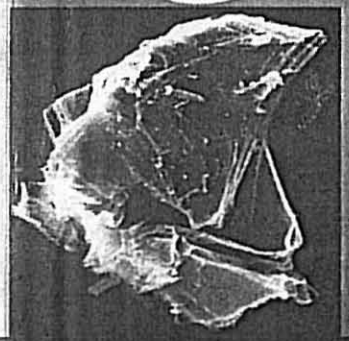

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TETRACARBONYL bis(μ-(2-METHYL-2-PROPANE-THIOLATO))DIIRIDIUM): A NEW CVD IRIDIUM PRECURSOR FOR THIN FILM DEPOSITION ON CARBON

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Deposits of noble metal and particularly Pt, Pd, Rh or Ir prepared by Chemical Vapor Deposition (CVD) are of special interest because of their low resistivity and high thermal stability. The major application is in microelectronics where they can replace gold as interconnects and contacts; other potential applications include protective coatings, gas sensors and catalysts. Among the noble metals cited above, iridium has been the subject of only a few studies, and suitable CVD precursors (i.e. volatile, easily synthesized, thermally stable during gas phase transport, characterized by a clean decomposition and non toxic) are relatively scarce. In this work, we report a new and simple synthesis of $[Ir(\mu\text{-}SC(CH_3)_3)(CO)_2]_2$ (tetracarbonyl bis(μ-(2-methyl-2-propane-thiolato))diiridium) and the preliminary studies of its use as precursor for OMCVD on planar carbon substrates.

Starting from IrI_4, the anion $[IrI_2(CO)_2]^-$ is formed after refluxing 15 h under a vigorous CO bubbling 200 mL of a DMF solution containing the 2 g of salt and 0.1 mL of water. During this time the colour of the solution turned from brown to yellow. A small amount of black precipitate formed during the reaction was removed by filtration. Excess solvent was removed under vacuum at 110°C to a final volume of 5 mL. Then 1 mL of 2-methyl-2-propanethiol was added under nitrogen at room temperature and the obtained solution stirred for 90 min. By addition of 300 mL of water at room temperature under nitrogen, a deep brown precipitate was formed. After filtration and drying under vacuum the yield on the desired complex is 60%.

This complex, stable to air and moisture, has been characterized by ^1H and ^{13}C NMR, FTIR and MS. The thermal stability of the precursor was investigated using thermogravimetric analyses coupled with mass spectrometry (TGA/DTA/MS) to 1000°C. The TGA analyses carried out in H_2 atmosphere show a 12% of additional mass loss compared to the TGA analyses under He atmosphere (53% against 65% of the initial mass, respectively). EDS

analysis of the residues obtained under He and H_2 atmosphere, revealed a significant contribution of sulfur in the sample obtained under He, but no sulfur on the one obtained under H_2.

In order to obtain iridium thin films with no sulfur contamination, CVD experiments were carried out using H_2 as reactive gas in a classic horizontal hot-wall type CVD reactor, with temperatures ranging from 150 to 450°C, over planar graphitic carbon oxidized with HNO_3. The carbon oxidation creates exchangeable carboxylic acid groups at the surface that will act as anchoring sites to metal deposition. The iridium precursor is vaporized at 120 °C under reduced pressure (10 Torr) for one hour in a stream of He (50 mL/min) as carrier gas. Hydrogen (50 mL/min) is introduced as the reactive gas in the middle of the decomposition zone, in close vicinity to the substrate. Iridium films were obtained and analysed by EDS in order to observe the influence of the temperature on the purity of the deposits (Figure 1).

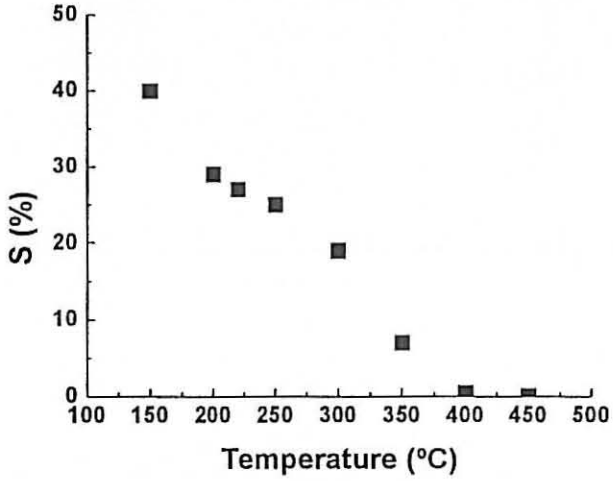

Figure 1 – Influence of the temperature on the sulfur content (atomic %, as measured by EDS) in the deposits.

At 400 °C, sulfur contamination was eliminated from the film. In order to bring down this temperature, platinum was used to assist precursor decomposition. However this strategy produced only minor improvements on the efficiency of complex decomposition, limiting for the present, the practical application of this technique.

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